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METHOD FOR THE PREPARATION OF MELAMINE

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BACKGROUND OF THE INVENTION1. Field of the Invention

The invention relates to a method for the preparation of melamine from urea in which melamine is recovered from a reaction product containing melamine by cooling the reaction product with a cooling medium in a supercritical state to obtain, without washing or further purification, a commercially usable high purity solid melamine product. More particularly the invention relates to a method for the preparation of melamine from urea via a continuous, anhydrous, high-pressure process in which melamine is recovered from a melamine melt by cooling the melamine melt through direct contact with a cooling medium in a supercritical state to obtain a high purity solid melamine product without further washing or purification. The product thus obtained is commercially valuable.

2. Description of the Related Art

A continuous, anhydrous, non-catalytic, high-pressure process for the production of melamine from urea is described in U.S. Patent No. 4,565,867, incorporated herein by reference. The patent describes the pyrolysis of urea in a reactor at a pressure of about 10.3 MPa to 17.8 MPa and a temperature of about 354°C to 427°C to produce a reaction product which contains liquid melamine, CO<sub>2</sub>, and NH<sub>3</sub>, and is transferred under pressure, as a mixed stream, to a gas-liquid separator unit. In the gas-liquid separator, which is kept at virtually the same pressure and temperature as the reactor, the reaction product is separated into gaseous and liquid streams. The gaseous

stream contains CO<sub>2</sub> and NH<sub>3</sub> off-gases and also melamine vapor while the liquid stream consists substantially of liquid melamine. The gaseous product is sent to a melamine scrubber, while the liquid melamine is transferred to a product cooler. In the melamine scrubber the above-mentioned CO<sub>2</sub> and NH<sub>3</sub> off-gases and melamine vapor, are scrubbed, at virtually the same pressure as the reactor pressure, with molten urea so as to pre-heat the urea, cool said off-gases and remove the melamine. The pre-heated urea, which contains the removed melamine, is then fed to the reactor. Meanwhile, in the product cooler, the pressure and temperature of the liquid melamine from the gas-liquid separator are reduced by means of a liquid cooling medium, preferably liquid ammonia, so as to produce a solid melamine product.

The drawback of this method is that the purity of the melamine obtained is typically in the range of 96 to 99.5%. Besides melamine, contaminants such as urea, CO<sub>2</sub>, ammeline-related compounds and other organic solids (melem and melam, for example) are present. The resulting purity of such a product is not high enough for some critical melamine applications, such as coatings. There is a need for a method to directly obtain, without further purification steps, higher purity melamine.

#### SUMMARY OF THE INVENTION

An object of the present invention is an improved method for the preparation of very high purity melamine, generally 99.5 to 99.95 wt. %, from urea in which the melamine is recovered from the urea pyrolysis reaction product as a dry powder. One particular object is an improved, continuous, high-pressure, anhydrous process for the production of melamine from urea in which very high purity melamine is obtained directly as a dry powder from the melamine melt through cooling.

These and other objects are achieved by the cooling of a reaction product comprising melamine by direct contact with a cooling medium which is in a supercritical state thereby obtaining a solid high purity melamine product.

The abovementioned and other objects of the present invention are achieved by a continuous, anhydrous, high-pressure process for recovering solid melamine from the reaction product of urea pyrolysis. This process can utilize a melamine scrubber unit, a reactor vessel, a gas-liquid separator unit, and a product cooler unit. The process can also optionally utilize either or both of a post-reactor vessel or an evaporator unit.

In such a process:

(1) Liquid urea melt is fed into the melamine scrubber unit at a pressure of about 5 to 25 MPa, preferably 8 to 20 MPa and at a temperature above the melting point of urea. In the scrubber the liquid urea comes into contact with off-gases from the gas-liquid separator unit. These off-gases are composed primarily of carbon dioxide and ammonia with small amounts of melamine vapor. The urea melt scrubs the melamine vapor out of the off-gas. The off-gases also pre-heat the urea melt prior to its transfer to the reactor vessel.

The carbon dioxide and ammonia gases are removed from the scrubber and are preferably sent to a urea plant for conversion to urea. The preheated urea melt, which now contains small amounts of melamine, is removed from the scrubber and fed to the reactor vessel.

The scrubber can be provided with a cooling jacket so as to ensure extra cooling. The scrubber can also be provided with internal cooling bodies.

(2) The urea and melamine melt is fed to the reactor vessel using, for example, a high-pressure

pump. Ammonia, either in the form of a liquid or hot vapor, is fed into the bottom of the reactor vessel for the purposes of promoting mixing in the vessel, preventing clogging of the vessel bottom, and preventing formation of melamine condensation products, for example, melam, melem and melone.

(3) The reactor vessel containing the urea melt, melamine, and ammonia is heated to a temperature of about 325°C to 450°C, preferably of about 350°C to 425°C, and pressurized to a pressure of about 5 to 25 MPa, preferably of about 8 to 20 MPa. Under these conditions, liquid melamine, gaseous carbon dioxide and more gaseous ammonia are produced from the pyrolysis of the urea melt. The melamine, carbon dioxide, and ammonia are fed as a mixed stream to the gas-liquid separator.

(4) In the gas-liquid separator the liquid melamine is separated from the gaseous ammonia and carbon dioxide and sent to, for example, a post-reactor vessel, an evaporator unit or a product cooler. The gaseous ammonia and carbon dioxide which also contain a small amount of melamine vapor are sent to the scrubber unit. The gas-liquid separator is preferably at the same temperature and pressure as the reactor vessel.

(5) In the post-reactor vessel the liquid melamine is further reacted with more ammonia under the same temperature and pressure conditions as are present in the reactor vessel. This second reaction with ammonia further reduces the impurity level in the melamine. After completion of this post-reaction the liquid melamine is sent to either an evaporator unit or a product cooler.

(6) In the evaporator unit the liquid melamine is converted to gaseous melamine. Any impurities remain in the evaporator unit while the gaseous melamine is transferred to a product cooler.

(7) In the product cooler the liquid or



gaseous melamine is cooled and solidified by contacting with a cooling medium in a supercritical state. The pressure during cooling of the liquid or gaseous melamine is preferably such that the reduced pressure is between about 0.9 and 2.5, more preferably between a reduced pressure of about 1 and the reactor pressure. The temperature during cooling is preferably such that the reduced temperature is between about 0.9 and 2, more preferably between about 1 and 1.5. The solid highly pure melamine is removed from the bottom of the cooling unit.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of an embodiment according to the present invention of a system for the production of melamine from urea which incorporates a post-reaction step prior to the cooling step.

Figure 2 is a flow diagram of an embodiment according to the present invention of a system for the production of melamine from urea which incorporates an evaporation step prior to the cooling step.

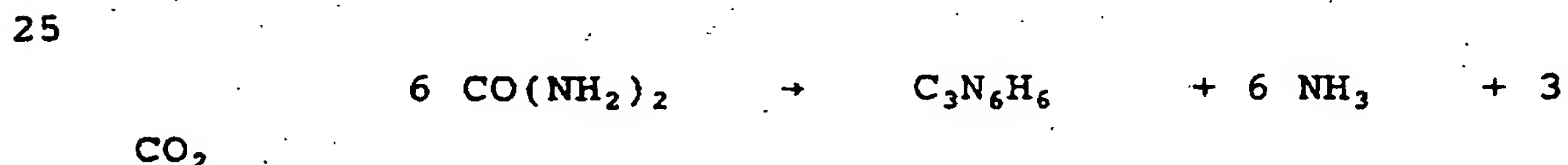
#### DETAILED DESCRIPTION OF THE INVENTION

We have now found that the purity of the melamine can be substantially increased by directly cooling the urea pyrolysis reaction product with a supercritical cooling medium. More particularly we have discovered that substantial increases in the purity of melamine can be obtained in the preparation of melamine from urea via a continuous, anhydrous, high-pressure process, in which melamine is recovered from the melamine melt leaving the urea pyrolysis reactor, by cooling the melamine melt through direct contact with a cooling medium which is in a supercritical state. Preferably, supercritical ammonia is used as the cooling medium. This cooling can be effected at a pressure that is virtually the same as or lower than

the urea pyrolysis reactor pressure, but generally higher than the critical pressure of the cooling medium. This method yields melamine having a purity, without further washing or purification, of greater  
5 than 99 wt. %, and more specifically having a purity of 99.5 to 99.95 wt. %.

The pressure and temperature of the cooling medium should be such that both the reduced pressure and temperature are about 0.9 or greater. Reduced  
10 pressure is defined as the ratio ( $P/P_c$ ) between the actual pressure ( $P$  in MPa) and the critical pressure ( $P_c$  in MPa) and reduced temperature is defined as the ratio ( $T/T_c$ ) between the actual temperature ( $T$  in °K) and the critical temperature ( $T_c$  in °K). Critical  
15 pressure is defined as the pressure of the liquid-vapor critical point. Critical temperature is defined as the temperature of the liquid-vapor critical point. For ammonia the critical pressure and temperature are 11.15 MPa and 408°K (135°C), respectively.

20 Urea, preferably in the form of a melt, is the preferred starting material for the production of melamine. Ammonia and carbon dioxide are by-products obtained during the melamine preparation, which proceeds according to the following reaction equation:



The preparation of the melamine can be  
30 carried out at low pressure, preferably between about 0.1 and 2.5 MPa, in the presence of a catalyst such as aluminum oxide, or at high pressure, preferably between about 5 and 25 MPa, without a catalyst. The temperature of the reaction varies between about 325°C and 450°C  
35 and preferably is between about 350°C and 425°C. The by-products ammonia and carbon dioxide are generally returned to an adjoining urea plant.



The results reported herein can be obtained in a plant suited for the preparation of melamine from urea. A plant suitable for the present invention can comprise a melamine scrubber, a reactor vessel, optionally in combination with a gas-liquid separator or with a separate gas-liquid separator, optionally a downstream post-reactor vessel and a product cooler. A general description of such a plant is presented in U.S. Patent No. 4,565,867 the complete description of which is incorporated herein by reference. The reactor can be a high pressure reactor, such as described in U.S. Patent No. 3,271,116, 3,470,163 or 3,432,274.

Preferably, in the method according to the invention a post-reactor vessel is used in which the melamine melt is contacted with ammonia, after which the post-reacted melamine is transferred to the product cooler, for cooling by means of direct contact with a cooling medium in a supercritical state. The advantage of incorporating a post-reaction step is that even lower amounts of by-products such as melem and/or melam are obtained, which results in a higher purity melamine product. Suitable post-reactor vessels are described in Nitrogen No. 139, September/October 1982, Fig. 3.

The flow diagram of Figure 1 illustrates an embodiment of the method. As shown, melamine can be prepared from urea in a plant comprising a melamine scrubber 1, a reactor vessel 2 which contains an internal gas-liquid separation unit 3, a post-reactor vessel 4, and a product cooler 5. Urea melt is fed to the gas scrubber 1 at a pressure of about 5 to 25 MPa, preferably 8 to 20 MPa and at a temperature above the melting point of urea. The gas scrubber 1 can be provided with a cooling jacket so as to ensure extra cooling. The melamine scrubber 1 can also be provided with internal cooling bodies. In the melamine scrubber 1 the liquid urea comes into contact with off-gases from the gas-liquid separation unit 3 of the reactor

vessel 2. These off-gases are composed primarily of carbon dioxide and ammonia with small amounts of melamine vapor. The urea melt scrubs the melamine vapor out of the off-gas and carries this melamine to the reactor vessel 2.

In the scrubbing process the off-gases are cooled down from about the temperature of the reactor 2, that is from about 350°C to 425°C, to about 175°C to 235°C, while the urea melt is heated to about 175°C to 235°C. Below the above-mentioned minimum temperatures ammonia and carbon dioxide can condense in the bottom of the melamine scrubber 1, which can result in the formation of ammonium carbamate, which can adversely affect the process. In order to prevent the detrimental formation of urea decomposition and/or condensation products, the melamine scrubber 1 temperature should, in general, not exceed about 275°C. The carbon dioxide and ammonia waste gases are removed from the top of the melamine scrubber 1 and are preferably returned to a urea plant for use as starting material.

The urea and melamine melt can then be withdrawn from the melamine scrubber 1 and fed, for example via a high-pressure pump, to the reactor vessel 2, which is at a pressure of about 5 to 25 MPa, and preferably of about 8 to 20 MPa. Gravity transfer of the urea melt can also be utilized by placing the melamine scrubber 1 above the reactor vessel 2.

In the reactor vessel 2 the molten urea is converted into melamine, carbon dioxide and ammonia by heating to a temperature of about 325°C to 450°C, preferably of about 350°C to 425°C, at a pressure of about 5 to 25 MPa, preferably of about 8 to 20 MPa.

Ammonia can be fed to the reactor vessel 2 in the form of a liquid or a hot vapor. The ammonia feed can serve as a purification agent to prevent clogging of the reactor vessel 2 bottom or to prevent the formation of melamine condensation products such as

melam, melem and melone, or to promote mixing in the reactor vessel 2. The amount of ammonia fed to the reactor is about 0.01 to 10 mol per mol urea; preferably, about 0.1 to 5 mol per mol urea, and in particular about 0.2 to 2 mol per mol urea. The carbon dioxide and ammonia formed in the reaction as well as any extra ammonia feed into the reactor vessel 2 can collect in an internal gas-liquid separation unit 3, for example in the top of the reactor vessel 2 and can be separated, in gaseous form, from the liquid melamine. As described above, the resulting gas mixture of carbon dioxide, ammonia and melamine is sent to the melamine scrubber 1 for removal of the melamine vapor and to preheat the urea melt. The liquid melamine is withdrawn from the reactor vessel 2 and transferred to a post-reactor vessel 4.

In the post-reactor vessel 4 the liquid melamine can again be contacted with about 0.01 to 10 mol ammonia per mol melamine and preferably about 0.1 to 2 mol ammonia per mol melamine. The contact time in the post-reactor vessel 4 is between about 1 minute and 3 hours, preferably between about 2 minutes and 1 hour. The temperature and pressure in the post-reactor vessel 4 are virtually the same as in the reactor vessel 2. After completion of the post-reaction step, the liquid melamine is discharged and transferred to a product cooler 5.

In the product cooler 5 the liquid melamine is cooled by contacting it directly with a cooling medium at a temperature and pressure at which the cooling medium is in a supercritical state. Preferably, supercritical ammonia is the cooling medium.

The pressure of the cooling medium during cooling of the liquid melamine is preferably such that the reduced pressure of the cooling medium is between about 0.9 and 2.5, more preferably between a reduced pressure of about 1 and the reactor pressure. The

temperature of the cooling medium during cooling is preferably such that the reduced temperature of the cooling medium is between about 0.9 and 2, more preferably between about 1 and 1.5.

5           The melamine is converted into a powder and removed from the bottom of the product cooler 5. The melamine powder has a melamine content of greater than 99 wt. %, and more specifically a melamine content of 99.5 to 99.95 wt. %, and can be used, generally,  
10 without further washing or purification, in applications which require very high purity melamine, such as coatings.

          In another embodiment of the method, a separate gas-liquid separation unit can be installed  
15 after the reactor vessel instead of internally to the reactor vessel.

          In yet another preferred embodiment of the method, as shown diagrammatically in Figure 2, an evaporation stage 6 is included between the post-  
20 reactor vessel 4 and the product cooler 5. In the evaporation stage liquid melamine melt is converted into gaseous melamine with any by-products remaining behind in the evaporator 6. According to this embodiment, gaseous melamine is then cooled in the  
25 product cooler 5 using a cooling medium in a supercritical state. This evaporation step has the advantage of further reducing the quantity of contaminating by-products and thus very high purity solid melamine is obtained. This may be advantageous  
30 especially in applications demanding a very high degree of purity.

          In another embodiment of the method, an evaporation stage can be included between the reactor vessel and the product cooler and the post-reaction  
35 stage can be bypassed.

          A method for the preparation of high purity melamine has been described in patent application

number 1002669 filed in the Netherlands on the date of March 21, 1996, the complete disclosure of which is hereby incorporated by reference.

The following non-limiting examples further describe the present invention.

### EXAMPLES

#### Example

The following example was carried out in a pilot plant equipped with a melamine scrubber, a reactor vessel incorporating a gas-liquid separator, a post-reactor vessel and a product cooler. The bottom of the post-reactor vessel was fed with 10 kg/h of ammonia at a temperature of 400°C and a pressure of 15 MPa. This ammonia flowed from the post-reactor vessel to the reactor vessel and from there, together with the ammonia and carbon dioxide formed during the melamine synthesis, to the melamine scrubber. The gas scrubber was fed with 100 kg/h of liquid urea at a temperature of 140°C and a pressure of 15 MPa. The liquid urea was heated to about 200°C in the melamine scrubber by means of the CO<sub>2</sub>, NH<sub>3</sub> and melamine off-gases from the reactor vessel, which were at a temperature of about 400°C. The melamine vapor entrained by the off-gases leaving the reactor vessel was removed from the off-gas by the urea melt and was transferred, together with the urea melt, to the reactor vessel. The urea and scrubbed melamine melt was reacted at a temperature of about 400°C and a pressure of about 15 MPa in the reactor vessel. The reaction product was separated into a gaseous and a liquid stream. The gaseous stream which was comprised of CO<sub>2</sub>, NH<sub>3</sub> and melamine vapor was sent to the melamine scrubber while the liquid stream of melamine was sent to the post-reactor vessel. In the post-reactor vessel the liquid melamine was contacted with ammonia for about 25 minutes at a temperature of about 400°C and a pressure of about 15 MPa. From the post-reactor the



liquid melamine was transferred to the product cooler, where it was cooled by mixing it with supercritical ammonia at a temperature of about 150°C and a pressure of about 14 MPa. A solid material of 99.7 wt. %  
5 melamine was obtained.

## WHAT IS CLAIMED IS:

1. A method for the preparation of melamine from a urea reaction product comprised of melamine comprising the step of:  
cooling said reaction product by direct contact with a cooling medium in a supercritical state to obtain a solid high purity melamine product.
2. A method according to claim 1, wherein said cooling medium is ammonia.
3. A method according to claim 2, wherein said ammonia is at a pressure during said cooling step which results in a reduced pressure of about 0.9 to 2.5.
4. A method according to claim 3, wherein said ammonia is at a pressure during said cooling step which results in a reduced pressure of about 1 to the reactor pressure.
5. A method according to claim 2, wherein said ammonia is at a temperature during said cooling step which results in a reduced temperature of about 0.9 to 2.
6. A method according to claim 5, wherein said ammonia is at a temperature during said cooling step which results in a reduced temperature of about 1 to 1.5.
7. A method according to claim 1, wherein said method further comprises the step of:  
reacting said reaction product with ammonia in a post-reaction step prior to said cooling step to produce a post-reaction product comprised of melamine.
8. A method according to claim 7, wherein said method further comprises the step of:  
evaporating said post-reaction product to form a gaseous post-reaction product comprised of

- melamine after said post-reaction step and prior to said cooling step.
9. A method according to claim 7, wherein said post-reaction step utilizes about 0.01 to 10 mol ammonia per mol melamine.
  10. A method according to claim 9, wherein said post-reaction step utilizes about 0.1 to 2 mol ammonia per mol melamine.
  11. A method according to claim 7, wherein said post-reaction step lasts for about 1 minute to 3 hours.
  12. A method according to claim 11, wherein said post-reaction step lasts for about 2 minutes to 1 hour.
  13. A method according to claim 1, wherein said method further comprises the step of:  
evaporating said reaction product to form a gaseous reaction product comprised of melamine prior to said cooling step.
  14. A method according to claim 1, wherein said melamine product has a purity of greater than 99% by weight.
  15. A method according to claim 14, wherein said melamine product has a purity of about 99.5 to 99.95% by weight.
  16. A continuous process for producing melamine from urea comprising the steps of:  
pyrolyzing urea in a reactor at a pressure from about 5 to 25 MPa and at a temperature from about 325 C to 450 C to produce a reaction product containing liquid melamine, gaseous carbon dioxide and gaseous ammonia;  
transferring said reaction product as a mixed stream to a gas-liquid separator unit;  
separating said reaction product in said gas-liquid separator unit into carbon dioxide and ammonia off-gases containing melamine vapor and liquid melamine;  
simultaneously transferring

- (a) said carbon dioxide and ammonia off-gases containing melamine vapor to a melamine scrubber unit and scrubbing said off-gases with molten urea to preheat said molten urea and cool said off-gases and remove therefrom said melamine vapor, and thereafter removing carbon dioxide and ammonia gases from said melamine scrubber unit and transferring said preheated molten urea containing said melamine to said reactor, and
- (b) said liquid melamine to a post-reactor vessel;

reacting said liquid melamine with ammonia in said post-reactor vessel to produce post-reacted liquid melamine;

transferring said post-reacted liquid melamine to a product cooler;

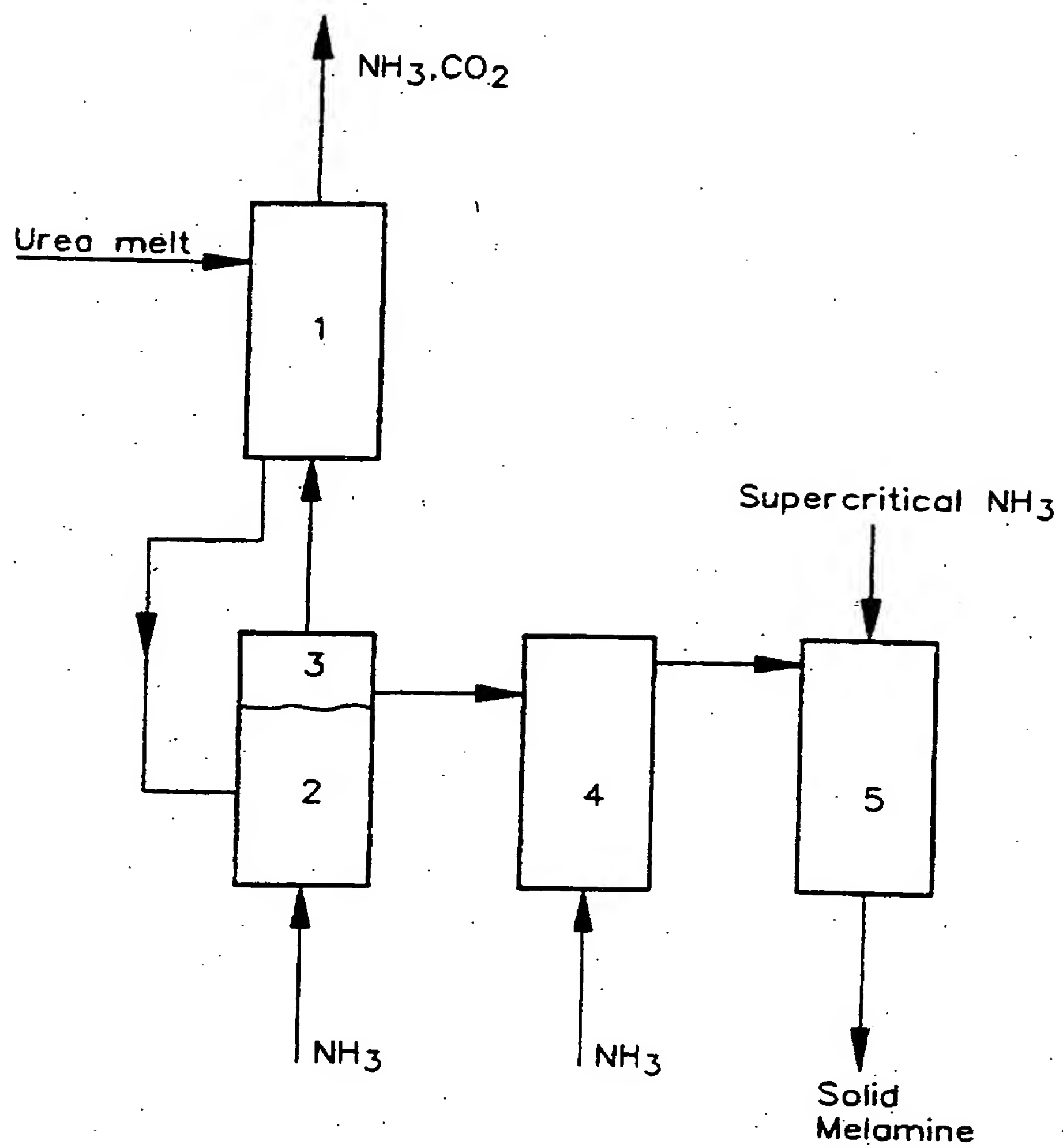
cooling said post-reacted liquid melamine by contacting it directly with a cooling medium which is in a supercritical state in said product cooler to produce a solid high purity melamine product; recovering said solid high purity melamine product.

- 17. In a continuous high-pressure process for producing melamine product by pyrolyzing urea to produce carbon dioxide, ammonia and melamine, the improvement, wherein the melamine is in the liquid phase, comprising, contacting said liquid melamine with a cooling medium which is in a supercritical state to obtain a solid melamine product, and recovering said melamine product without further washing or purification as a solid containing about 99.5 to 99.95% by weight melamine.
- 18. A process according to claim 17, wherein said cooling medium is ammonia.
- 19. A continuous process for producing melamine from urea comprising the steps of:

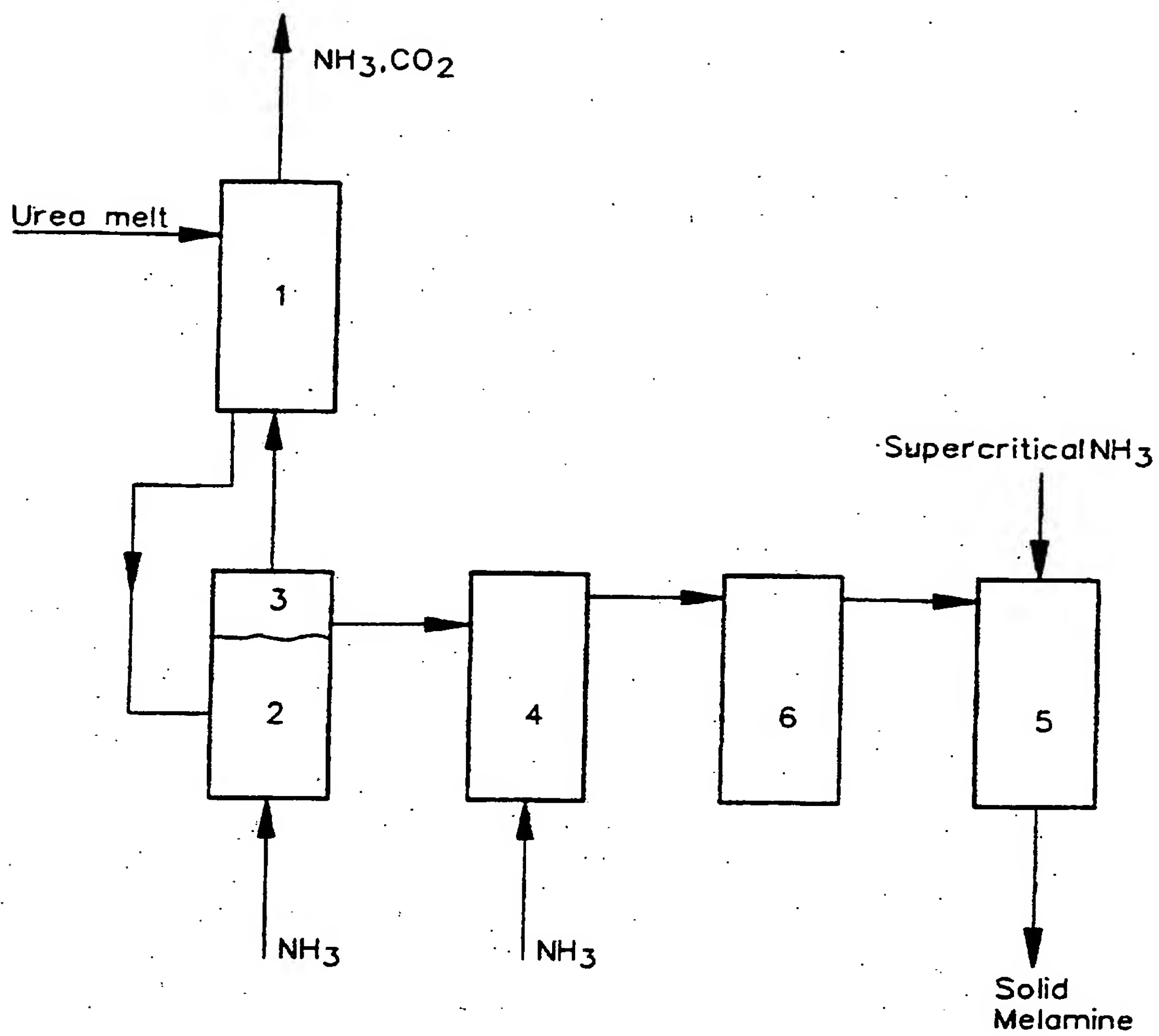
pyrolyzing urea in a reaction zone at a high pressure and high temperature to produce a reaction product comprising liquid melamine, gaseous carbon dioxide and gaseous ammonia; reacting said liquid melamine with ammonia in a post-reaction zone to produce post-reacted liquid melamine; cooling said post-reacted liquid melamine by contacting it directly with a cooling medium which is in a supercritical state in a product cooler to produce a solid high purity melamine product.



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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL 97/00146

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07D251/60 C07D251/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 565 867 A (THOMAS ROGER E ET AL) 21 January 1986 see the whole document & NL 8 403 843 A	1-12
P,X	US 5 514 796 A (BEST DAVID ET AL) 7 May 1996 see the whole document	1-12
P,X	WO 96 20182 A (AGROLINZ MELAMIN GMBH) 4 July 1996 see claim 1	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 June 1997

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

I. International Application No

PCT/NL 97/00146

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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